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2.*** shows the word which can not be translated.

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CLAIMS

(57) [Claim(a)]

[Claim 1(a)] A polymer whose substantial repeating unit it has a reactive silicon group and is -
 $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-$, (b) A bisphenol A type epoxy resin, a silane coupling agent which contains an amino group and alkoxy silyl groups in one molecule (c), (d) A hardenability resin composite which consists of an epoxy resin hardener which is a silanol condensation catalyst which is a tin compound containing tetraivalent tin and the (e) third class amine compound, or its salt.

[Claim 2(a)] The hardenability resin composite according to claim 1, wherein a main chain of a polymer of an ingredient is polyether obtained from a tetrahydrofuran by ring opening polymerization, or polyether obtained from a tetrahydrofuran and cyclic ether by ring opening polymerization.

[Claim 3(b)] The hardenability resin composite according to claim 1 or 2, wherein an ingredient is an

epichlorohydrin bisphenol A type epoxy resin obtained from bisphenol A and epichlorohydrin.
 [Claim 4(c)] A hardenability resin composite given in any 1 clause of Claims 1-3 to which a blending ratio of a silane coupling agent of an ingredient is characterized by being 0.01 - 50 weight section to (a) ingredient to be mixed.

[Claim 5(d)] A hardenability resin composite given in any 1 clause of Claims 1-4 to which a blending ratio of an epichlorohydrin bisphenol A type epoxy resin of an ingredient is characterized by being 0.01 - 20 weight section to (a) ingredient to be mixed.

[Claim 6(e)] A hardenability resin composite given in any 1 clause of Claims 1-5 to which a blending ratio of an epoxy resin hardener of an ingredient is characterized by being 0.01 - 300 weight section to (b) ingredient to be mixed.

[Claim 7(a)] A method of phase structure of a hardened material facing controlling phase structure of a hardened material produced by making harden the hardenability resin composite according to claim 1, and changing an addition of a silane coupling agent.

[Claim 8(c)] A method of carrying out 0.01-50 weight-section addition of the silane coupling agent of an ingredient to polymer 100 weight section of the (a) ingredient according to claim 7.

[Translation done.]

monocoum [such as dieth oxyethylene], a butylamine, octylamine, lauryl amine, dibutylamine, monocoum [such as dieth oxyethylene], triethanolamine, diethylenetriamine, Trichloroethylene, oxyethylene, benzylamine, diethylamine propylamine, xylene diamine, a triethylenediamine, guanidine, dihydroxyethylene, 2,4,6-tris(dimethylamino)phenol, morpholine, Aniline compounds, such as N-methyl-morpholine, 2-ethyl-4-methylimidazole, 1- and 8-azabicyclo [5.4.0] undecene 7 (DBU), or salt [with carboxylic acid of these amine compounds, etc.] - low molecular-weight-polyamide resin, obtained from superfluous polyamine and polyacidic acid, although a resultant of superfluous polyamine and an epoxy compound, etc. are illustrated. Not a thing limited to these but a condensation catalyst currently generally used can be used. These silanol condensation catalysts may be used alone and may be used together two, or more stars. A concomitant use system of organic metallic compounds or organic metallic compounds, and an amine compound is preferred from a point of hardenability among these silanol condensation catalysts. Especially, a tetraavalent organotin compound is preferred also in organotin compounds, and when a tetraavalent organotin compound and a compound which has an amino group of an amino group especially the first aliphatic organotin compound and a hydroxylic silane group as a (c) ingredient are used together, it becomes what was excellent in especially an epoxy resin composition of a hardened material.

[0028](d) On the addition of the 0.01-100 copies of the (d) ingredients, the crosslinking reaction of the polymer which has a reactive silanol is 0.5-100% which is the (a) ingredient in the case of less than 0.01 copy becomes insufficient and it exceeds 100 copies, it is possible to have an adverse effect on an adhesive property etc., and is not desirable.

[0029](e) An epoxy resin hardener of the (e) ingredient contained in this invention, Triethylenetetramine, tetraethylenetetramine, diethylamine propylamine, N-aminoethyl piperazine, MENSENJ 3Amin, isopropylendiamine, Morpholine, piperidine, m-xylene diamine, m-phenylenediamine, The first classes, such as diaminodiphenylmethane and diaminodiphenyl sulfone, The second class amines, Triethylamine, N-methyl-morpholine, N, N'-dimethylpiperazine, Pyridine, piperidine, guanidine, dihydroxyethylene, 1,8-diazabicyclo [5.4.0] undecene 7 (DBU), Benzyl(dimethylamino) phenol, 2-(dimethyl aminoethyl) phenol. The third class amines, such as 2,4,6-tris(dimethylamino)phenol, And the organo acid acid, 2-methylimidazole, 2-ethyl-4-methylimidazole, Imidazole-derivatives: polyamide resin, diorganodis: boron trifluoride-amine complexes, such as 2-undecyloxyimidazole and 1-benzyl-2-methylimidazole; Phthalic anhydride, hexahydro phthalic anhydride, tetrahydro phthalic anhydride, And methylene tetrahydro phthalic anhydride, a dodecylsuccinic anhydride, Anhydrous carboxylic acid, alcohols: phenols: carboxylic acid, such as trimellitic anhydride, pyromellitic dianhydride, and anhydrous KURONEN acid; Boron trifluoride, Lewis acids, such as phosphorus pentachloride, trichloro aluminum, and a tin tetrachloride, Generally used bases, etc. are illustrated. It is not limited to these, and these epoxy resin compositions, preferably used can be used. These epoxy resin hardeners may be used alone and may be used together two or more stars. The third class amines and its organo acid acid, and imidazole derivatives are preferred from a point of the hardenability and its epoxy resin hardness.

[0030](f) What is necessary is just to use it according to the purpose to 100 copies of (f) ingredients in 0.01-300 copies, although an addition of an ingredient changes with the kind and kinds of epoxy resin of the (b) ingredient.

[0031](a) There is no limitation in the method of preparation of a hardenable resin composition containing an ingredient, the (c) ingredient, the (d) ingredient, and the (e) ingredient. For example, the (a) ingredient, the (c) ingredient, the (d) ingredient, and the (e) ingredient are blended, it multi using a mixer, a roll or a kneader, or each ingredient is dissolved using a suitable solvent, a usual method of mixing is adopted, and it gets. It is also possible by combining each ingredient suitably to build and use a liquid type and a two-component compound.

[0032]In a constituent of this invention, further I needed A dehydrator, a computerizer, an adhesive improving agent. Various additive agents, such as a physical-properties regulator, a preservation stability improving agent, a bulking agent, an antistatic agent, an ultraviolet ray absorbent, a metal deactivator, an antioxidant, light stabilizer, mine system radical chain inhibitor, a phosphorus system peroxide decomposition inhibitor, lubricant, pigments, and a tanning agent, can be added suitably.

[0033]When using a bulking agent as an additive agent, for example, wood flour, wettable carbon, clay powder, Pulp, a cotton cloth, mica, graphite, carbon black, kaolin, A carbonaceous titanium oxide, an aluminum powder, and the end of this in this, this silanol condensation nature silanol, a silicic acid anhydride, and this sort of quartz powder. These bulking agents may be used independently and may be used together two or more stars.

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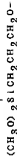
[0034]Other polymers which have a reactive silicon group other than a polymer of the (a) ingredient, for example, reactive silicon group content polypropylene oxide, other reactive silicon group content polyether, a polydimethyl siloxane, etc., may be added.

[0035]A hardenable resin composition of this invention is excellent in an adhesive property. A hardened material of a rate of high elasticity which raised cohesive force of not only a hardened material of high elongation but a matrix with a low elastic modulus, and high tension shear strength can be obtained by changing an addition of a silane coupling agent. Therefore, it can use to the dynamic characteristic demanded as adhesives which can respond, a sealing compound, and a binder by an easy means referred to as changing an addition of a silane coupling agent.

[0036]Working example1This invention is explained still more concretely based on an embodiment.

300 g of polytetramethylene glycol of the example of manufacture 1 hydroxy value 273 and the average molecular weight 4,110 are put into 1-4 autoclave. After adding 46.5 g of CH₃ONa28% methanol solution and carrying out decomposition degassing at 130 °C for about 6 hours, a 24-methyl chloride was dropped and was made to react for about 2 hours. It was checked that the epoxy groups were 80% of whole ends by iodine value method. The reaction mixture was cooled to 20 °C, and polytetramethylene oxide into a 300-ml 4-mouth flask. 100mccol Adding the 10% ethanol solution of chloroacetic acid and dropping methyl dimethylsiloxane at 50 °C, it was made to react at 80 °C for about 3 hours. ¹H-NMR measurement [0037]

[Chemical formula 4]



It was checked that polytetramethylene oxide of the average molecular weight 4,400 [about] which has 1.8 structures per molecule had been obtained.

Using the tetrahydrofuran propylene oxide random copolymer of the example of manufacture 2 hydroxy value 280, the average molecular weight 4,007, and 10 weight % of propylene oxide contents, by the same method as the example of manufacture. The tetrahydrofuran propylene oxide random copolymer of the average molecular weight 4,300 [about] which has 1.8 structures per molecule expressed with an end of the above-ization 4 was obtained.

The average molecular weight which introduced the example of manufacture 3 allyl ether end into 90% of whole ends uses the tetrahydrofuran propylene oxide random copolymer whose propylene oxide content is 10 weight % in 8,600. The tetrahydrofuran propylene oxide random copolymer of the average molecular weight 6,800 [about] which has 1.4 structures per molecule which hydrolyzates by the same method as the example of manufacture, and are expressed with an end by the above-ization 4 obtained.

An average molecular weight, which introduced the example of manufacture 4 allyl ether end into 90% of whole ends uses the tetrahydrofuran propylene oxide random copolymer whose propylene oxide content is 10 weight % in 8,200. A tetrahydrofuran propylene oxide random copolymer of the average molecular weight 8,400 [about] which has 1.8 structures per molecule which hydrolyzates by the same method as the example 1 of manufacture, and are expressed with an end by the above-ization 4 was obtained.

A polytetramethylene oxide random copolymer of polytetramethylene oxide triblock copolymer of the example of manufacture 5 hydroxy value 287, the average molecular weight 3,910, and 90 weight % of propylene oxide contents is used. A polytetramethylene oxide random copolymer of polytetramethylene oxide triblock copolymer of the average molecular weight 4,100 [about] which has 1.8 structures per molecule expressed with an end by the above-ization 4 by the same method as the example 1 of manufacture was obtained.

Polypropylene oxide of the average molecular weight 5,000 which introduced an example of manufacture 6 allyl ether end into 97% of whole ends is used. Polypropylene oxide of the average molecular weight 5,200 [about] which has 1.7 structures per molecule which hydrolyzates by the same method as the example 1 of manufacture, and are expressed with an end by the above-ization 4 was obtained.

Polytetramethylene oxide of the average molecular weight 4,400 which has the reactive silicon group obtained in Embodiments 1-3, the comparative examples 1- the example 1 of 2-phenyl-2-propyl-2-propyl-Epoxy #528 (of recovery after epoxy company male and an epoxide number 11.02 (Nippon Unicar make) resin), the weight per epoxy equivalent about 180 and the bonding agent #1122 (Nippon Unicar make) gamma-(2-aminophenyl) amonopropyl trimethoxysilane and silanol condensation catalyst #818 (the Sanjyo Organic

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ランキャップ リング等の 加工 (参照図)		ランキャップ硬化					硬化率 (%)
		M ₅₀	M ₅₀	M ₁₀₀	T	B	
		(kg/t/cm ³)	(kg/t/cm ³)	(kg/t/cm ³)	(kg/t/cm ³)	(kg/t/cm ³)	(%)
比較例1	0	3.5	4.6	8.1	107	515	61.9
実施例1	1	10.4	15.9	31.6	81.9	224	98.7
実施例2	2	21.9	32.7	59.6	90.5	158	147
実施例3	5						142
実施例4	7.5						143
比較例2	0	10.4	16.0	32.3	128	310	51.7
実施例5	1	34.6	50.2	-	57.5	71	115
実施例6	2	86.9	114	-	116	51	165
実施例7	5						128
実施例8	7.5						116
比較例3	0	3.5	5.4	27.4	460	21.1	
実施例9	1	7.1	13.6	62.5	290	93.8	
比較例4	2	10.7	21.2	68.2	250	100	

[0042]

Table 3)

使用 量割合		ランキャップ硬化					硬化率 (%)
		M ₅₀	M ₁₀₀	T	B	E	
		(kg/t/cm ³)	(kg/t/cm ³)	(kg/t/cm ³)	(kg/t/cm ³)	(kg/t/cm ³)	(%)
実施例2	比較例1	32.7	59.6	90.5	158		147
実施例9	比較例2	36.9	64.4	77.7	125		180
実施例10	比較例3	27.4	46.3	74.4	180		100
実施例11	比較例4	24.9	41.8	112	314		143
実施例12	比較例5	37.9	67.1	121	189		92
比較例5	比較例6	10.7	21.2	68.2	250		100

3) After it used as the frozen ultra thin section the hardened material obtained by the transmission electron microscope observation above-mentioned examination 1 and cinnic acid dyed it, transmission electron microscope observation was performed with the accelerating voltage of 200 kV using the transmission electron microscope (the JEOL Co. Ltd. make, JEM-2000FX).

[0043] The comparative example 1 was shown in Embodiment 9 and drawing 3, and the transmission electron microscope observation photograph of the comparative example 4 was shown in drawing 1 at drawing 4, at Embodiment 2 and drawing 2.

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[0040] While the tensile shear strength is higher than it can set to a comparative example in the embodiment of this invention so that more clearly than Table 2, the modulus of the hardened material changes a lot with the increase in the addition of a silane coupling agent.

[0045] The hardened material of the constituent using the various polymers of the (a) ingredient contained in this invention is a high modulus from it of a comparative example so that more clearly than Table 3. High cohesive force is shown.

[0046] In the transmission electron microscope observation images of Embodiment 2 shown in drawing 1, compared with the thing of the comparative example 1 shown in drawing 3, the particle diameter of the particle state domain considered to be the hardened epoxy resin which is dyed with cinnic acid becomes small. And it is suggested that the volume ratio of a domain and a matrix is smaller than the composition ratio (50/100) of the epoxy resin and resinous silicon group content polymer in a constituent, and there are many kinds of species and sizes of the particle state domain. It is suggested that the particle state domain of the hardened material of the different size as a high modulus. It is clear by carrying drawing 1 (embodiment 2) and drawing 2 (embodiment 9) with the transmission electron microscope observation images of drawing 4 (comparative example 4) that to be observed by the thing using the various polymers of the (a) ingredient contained in this invention.

[0047]

[Effect of the invention] According to this invention, the hardenable resin composite excellent in the adhesive property is provided. The hardened material of the rate of high elasticity which raised the cohesive force of not only the hardened material of high elongation but the matrix with the low elastic modulus, and high tension shear strength can be obtained by controlling the addition of a silane coupling agent.

[0048] The hardenable resin composite of this invention can be used to the dynamic characteristic demanded as the adhesives which can respond, a sealant, and a binder by the easy means referred to as changing the addition of a silane coupling agent.

[Translation done.]

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings.]

[Drawing 1] It is a transmission electron microscope observation photograph which shows the phase structure of the hardened material obtained from the constituent of Embodiment 2 of this invention.

[Drawing 2] It is a transmission electron microscope observation photograph which shows the phase structure of the hardened material obtained from the constituent of Embodiment 9 of this invention.

[Drawing 3] It is a transmission electron microscope observation photograph which shows the phase structure of the hardened material obtained from the constituent of the comparative example 1.

[Drawing 4] It is a transmission electron microscope observation photograph which shows the phase structure of the hardened material obtained from the constituent of the comparative example 4.

[Translation done.]

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(73) 特許権者 000000941

錦澤化学工業株式会社

大阪府大阪市北区中之島3丁目2番4号

(72) 発明者 服部 準

高砂市高砂町沖浜町2番83号

(72) 発明者 棚田 朝夫

加古川市別府町新野辺北町5-105

(74) 代理人 100058225

弁理士 葛田 瑠子 (外1名)

審査官 原田 隆美

最終頁に続く

(54) 【発明の名称】 硬化性樹脂組成物

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(57) 【特許請求の範囲】

【請求項1】 (a) 反応性ケイ素基を有し、実質的な繰返し単位が

$$-CH_2-CH_2-CH_2-CH_2-O-$$

である重合体、

(b) ビスフェノールA型エポキシ樹脂、

(c) 1分子中にアミノ基とアルコキシシリル基を含有するシランカップリング剤、

(d) 4価のスズを含有するスズ化合物であるシラン-シラン縮合触媒、及び

(e) 三級アミン化合物またはその塩であるエポキシ樹脂硬化剤

よりなる硬化性樹脂組成物。

【請求項2】 (a) 成分の重合体の主鎖が、テトラヒドロフランから開環重合により得られるポリエーテル、あ

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るいはテトラヒドロフランと環状エーテルとから開環重合により得られるポリエーテルであることを特徴とする請求項1記載の硬化性樹脂組成物。

【請求項3】 (b) 成分が、ビスフェノールAとエポキシロリンより得られるエポキシロリン-ビスフェノールA型エポキシ樹脂であることを特徴とする請求項1又は2記載の硬化性樹脂組成物。

【請求項4】 (c) 成分のシランカップリング剤の配合割合が、(a) 成分100重量部に対して0.01~50重量部であることを特徴とする請求項1~3のいずれか1項に記載の硬化性樹脂組成物。

【請求項5】 (d) 成分のシラン-シラン縮合触媒の配合割合が、(a) 成分100重量部に対して0.01~20重量部であることを特徴とする請求項1~4のいずれか1項に記載の硬化性樹脂組成物。

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